



US005395925A

United States Patent [19][11] **Patent Number:** **5,395,925****Koch et al.**[45] **Date of Patent:** **Mar. 7, 1995**

[54] **ASYMMETRIC SULFO
GROUP-CONTAINING DISAZO
COMPOUNDS CONTAINING TWO
6-HALO-1,3,5-TRIAZINYL GROUPS**

1405016 9/1975 United Kingdom 534/634
1461125 5/1977 United Kingdom 534/634
2008144 5/1977 United Kingdom 534/634

[75] Inventors: **Werner Koch**, Oberwil, Switzerland;
Kurt Brenneisen, Grenzach-Wyhlen,
Germany

[73] Assignee: **Sandoz Ltd.**, Basle, Switzerland

[21] Appl. No.: **30,929**

[22] Filed: **Mar. 12, 1993**

Related U.S. Application Data

[63] Continuation of Ser. No. 483,146, Feb. 21, 1990, abandoned, which is a continuation of Ser. No. 160,954, Feb. 26, 1988, abandoned, which is a continuation of Ser. No. 916,910, Oct. 9, 1986, abandoned, which is a continuation-in-part of Ser. No. 503,320, Jun. 10, 1983, abandoned, which is a continuation of Ser. No. 306,881, Sep. 30, 1981, abandoned.

Foreign Application Priority Data

Oct. 7, 1980 [GB] United Kingdom 8032278

[51] Int. Cl.⁶ **C09B 62/09; C09B 67/22;**
D06P 1/382

[52] U.S. Cl. **534/634; 8/549**

[58] Field of Search 534/624, 634; 8/549

References Cited**U.S. PATENT DOCUMENTS**

3,118,869 1/1964 Berrie et al. 534/634 X
3,226,176 12/1965 Hindermann et al. 534/634 X
3,646,002 2/1972 Andrew et al. 534/634 X
3,647,778 3/1972 Andrew et al. 534/634 X
4,082,739 4/1978 Seitz 534/634 X
4,148,790 4/1979 Sueda et al. 534/634 X
4,228,071 10/1980 Riat et al. 534/634 X
4,323,497 4/1982 Hoyer et al. 534/634 X
4,502,866 3/1985 Brenneisen et al. 534/624 X
5,032,142 7/1991 Egger et al. 8/549

FOREIGN PATENT DOCUMENTS

2611550 9/1976 Germany 534/634
51-147688 12/1976 Japan 534/634
785222 10/1957 United Kingdom 534/634
854432 11/1960 United Kingdom 534/634

OTHER PUBLICATIONS

English translation of JP 51-147688 Imahori et al.

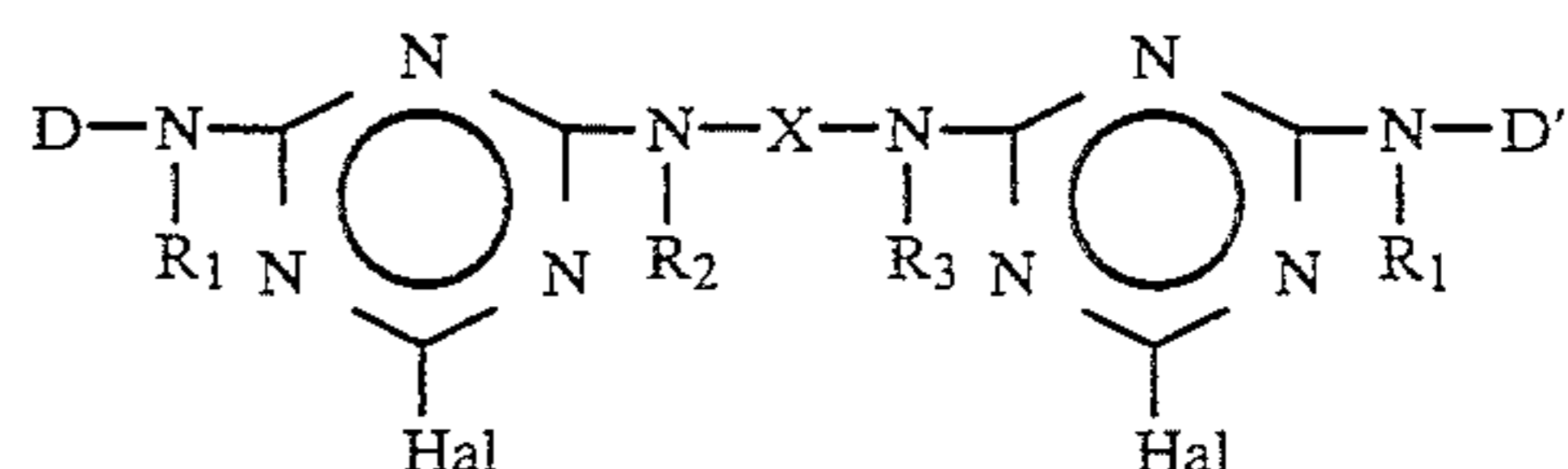
Primary Examiner—Mary C. Lee

Assistant Examiner—Fiona T. Powers

Attorney, Agent, or Firm—Robert S. Honor; Melvyn M. Kassenoff

[57] ABSTRACT

Compounds of the formula



wherein

D is the residue of a metal-free azo dye free of fiber-reactive groups and containing 2 to 4 sulfo groups,

D' is the residue of a metal-free azo dye free of fiber-reactive groups and containing 2 to 4 sulfo groups, with the proviso that D and D' are different,

each R₁ is independently hydrogen or C₁₋₄alkyl,

each of R₂ and R₃ is independently hydrogen, C₁₋₄alkyl or 2-, 3- or 4-hydroxy(C₂₋₄alkyl),

X is linear or branched C₂₋₁₀alkylene or linear or branched C₃₋₁₀alkylene monosubstituted or disubstituted by hydroxy which optionally contains one or two radicals selected from —O— and —NR_a—, wherein R_a is hydrogen or C₁₋₄alkyl, and

each Hal is fluoro, chloro or bromo, which compounds are in free acid or salt form, and mixtures thereof, which compounds and mixtures are useful as fiber-reactive dyes for dyeing and printing hydroxy group- and/or nitrogen-containing organic substrates, for example, leather and textiles containing or consisting of natural or synthetic polyamides such as wool, silk and nylon and natural or regenerated cellulose such as cotton, viscose and spun rayon.

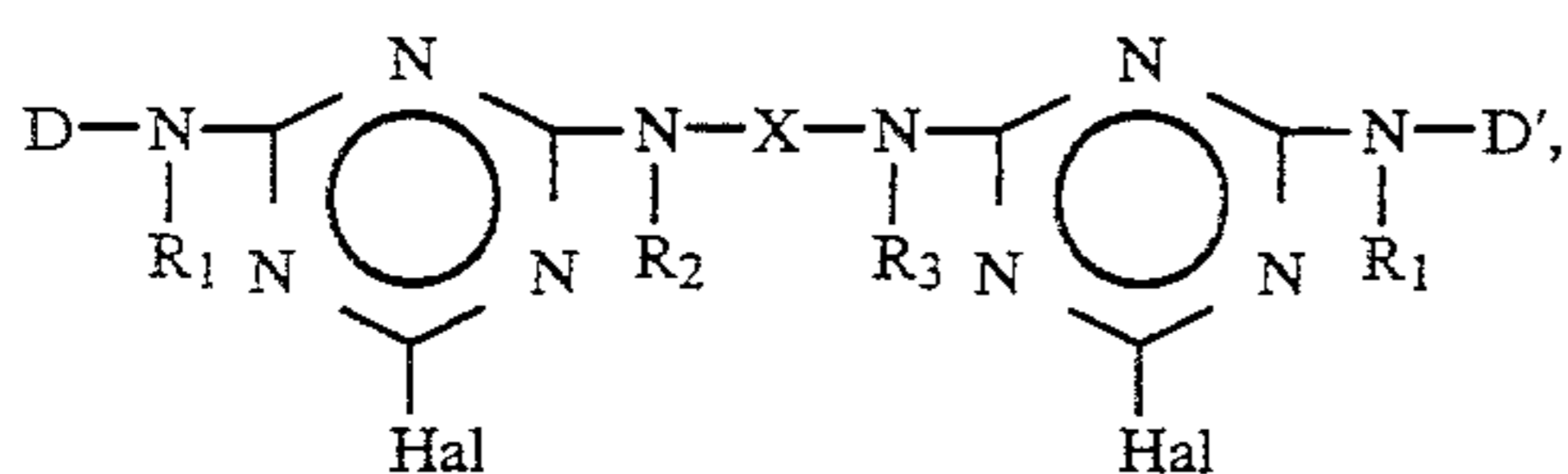
20 Claims, No Drawings

**ASYMMETRIC SULFO GROUP-CONTAINING
DISAZO COMPOUNDS CONTAINING TWO
6-HALO-1,3,5-TRIAZINYL GROUPS**

This is a continuation of application Ser. No. 07/483,146, filed Feb. 21, 1990, now abandoned, which in turn is a continuation of application Ser. No. 07/160,954, filed Feb. 26, 1988, now abandoned, which in turn is a continuation of application Ser. No. 06/916,910, filed Oct. 8, 1986, now abandoned, which in turn is a continuation-in-part of application Ser. No. 06/503,320, filed Jun. 10, 1983, now abandoned, which in turn is a continuation of application Ser. No. 06/306,881, filed Sep. 30, 1981, now abandoned.

The present invention relates to halotriazinyl-containing compounds, their production and use as fibre-reactive dyestuffs.

More particularly, the present invention provides asymmetric compounds of formula I,



in which D is the residue of a metal-free azo dye free of fibre-reactive groups and containing 2 to 4 sulfo groups,

D' has one of the significances of D, with the proviso that D and D' are different,

each R₁ is independently hydrogen or C₁₋₄alkyl,

each of R₂ and R₃ is independently hydrogen, C₁₋₄alkyl or 2-, 3- or 4-hydroxy(C₂₋₄alkyl),

X is a monohydroxy- or dihydroxy-substituted straight chain or branched chain C₃₋₁₀-alkylene radical which optionally contains one or two hetero atom-linkages selected from —O— and

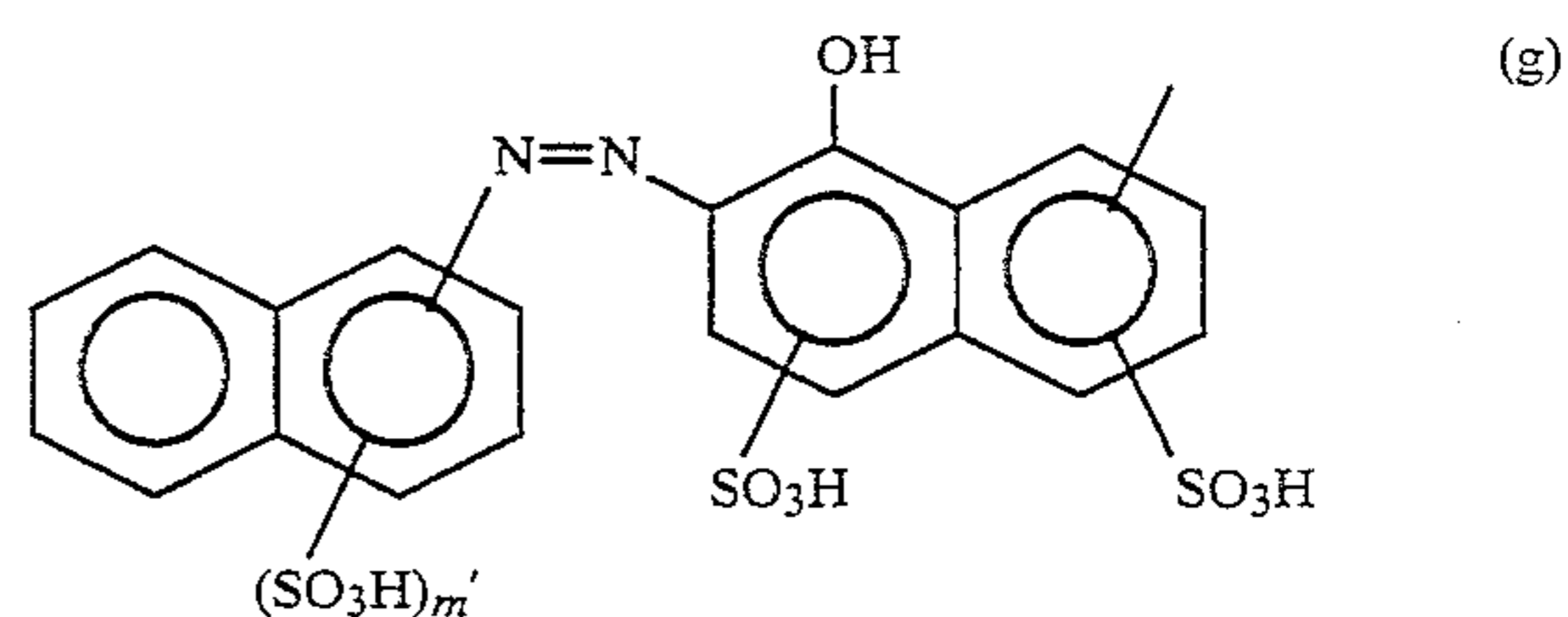
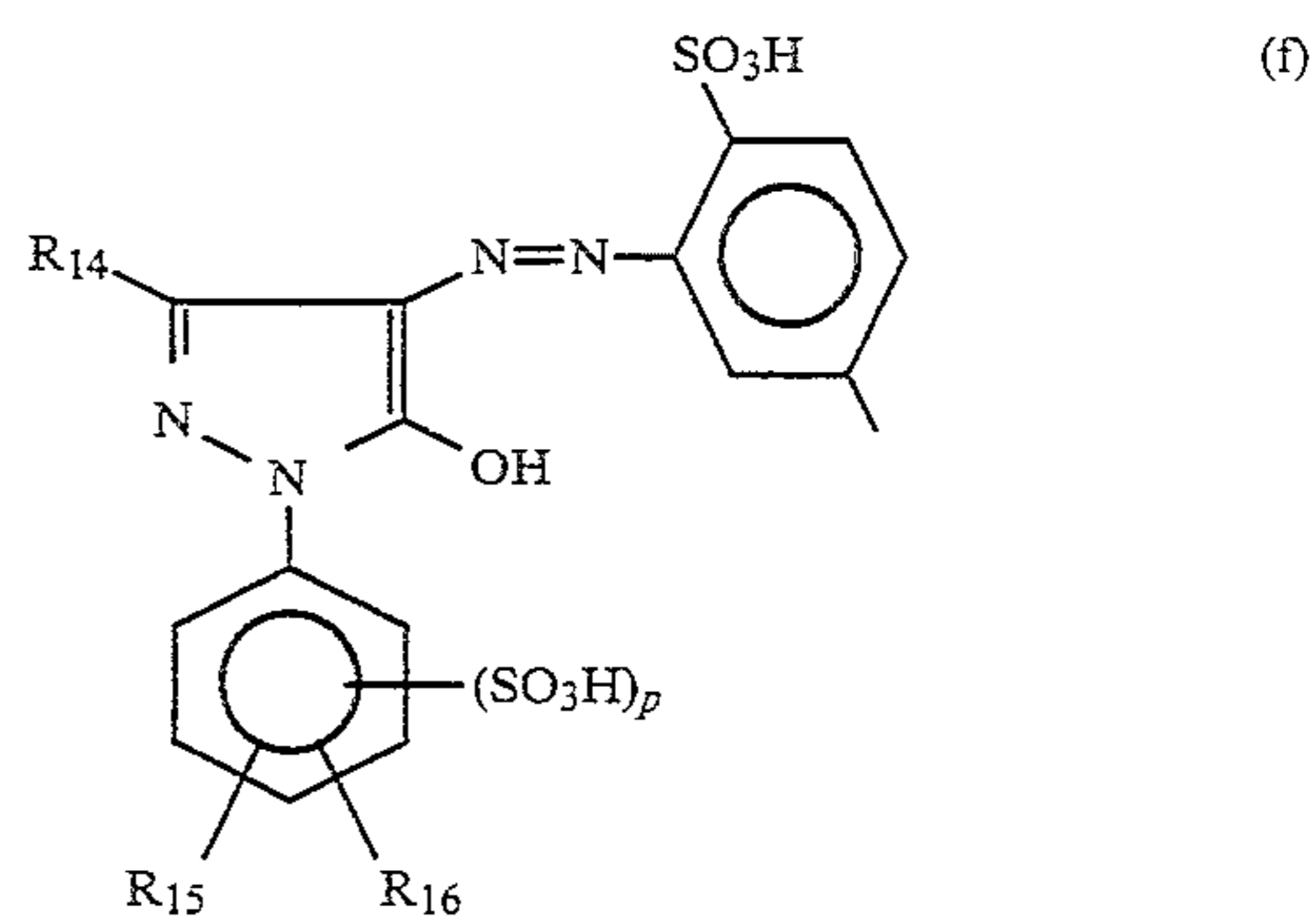
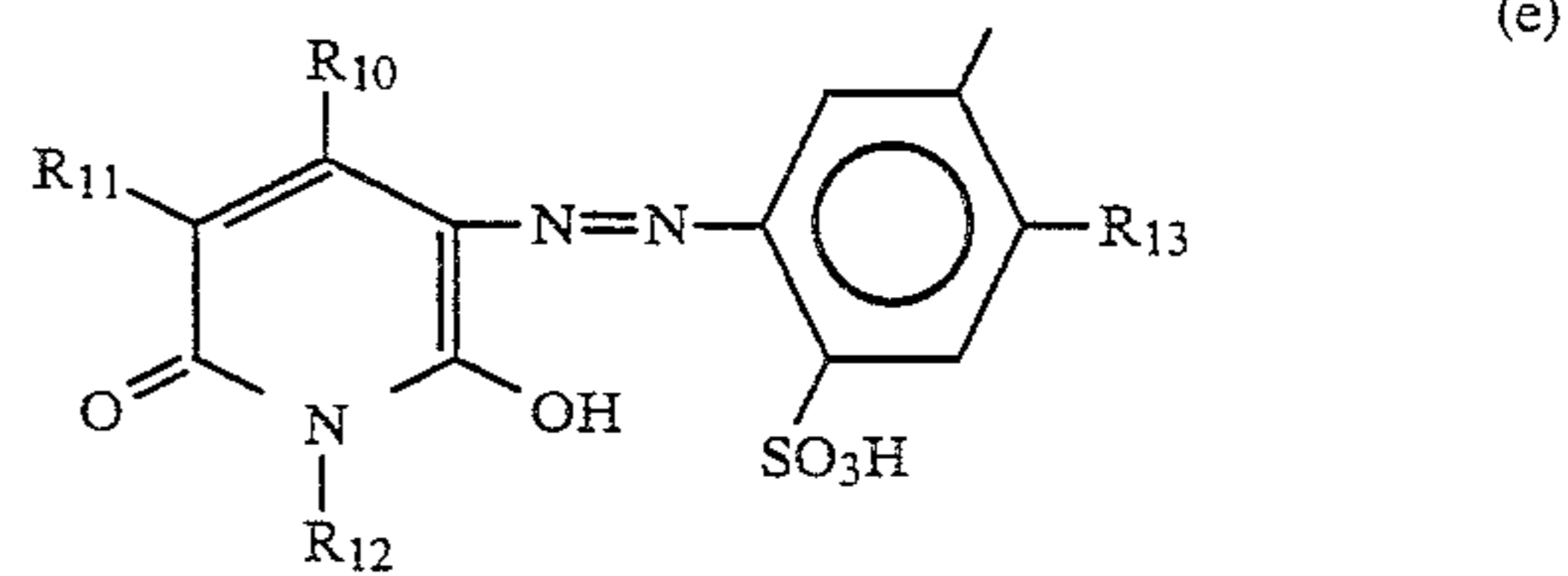
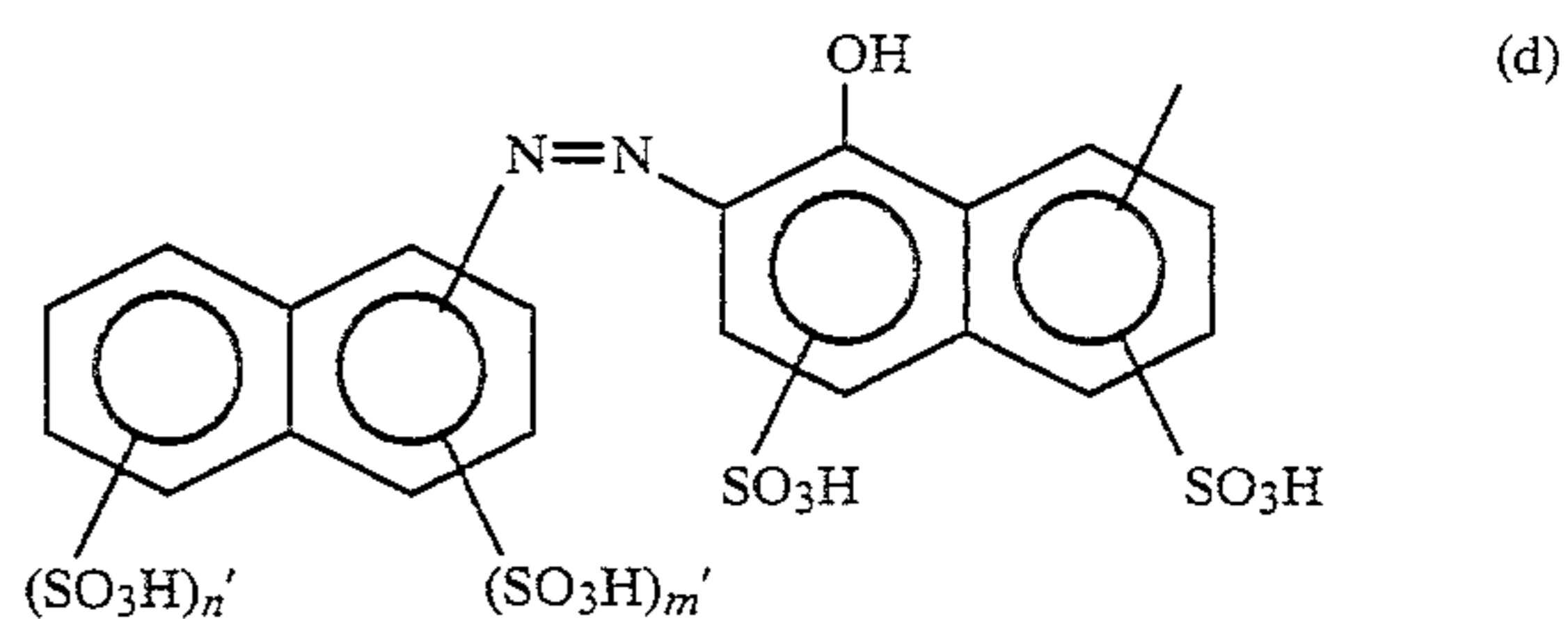
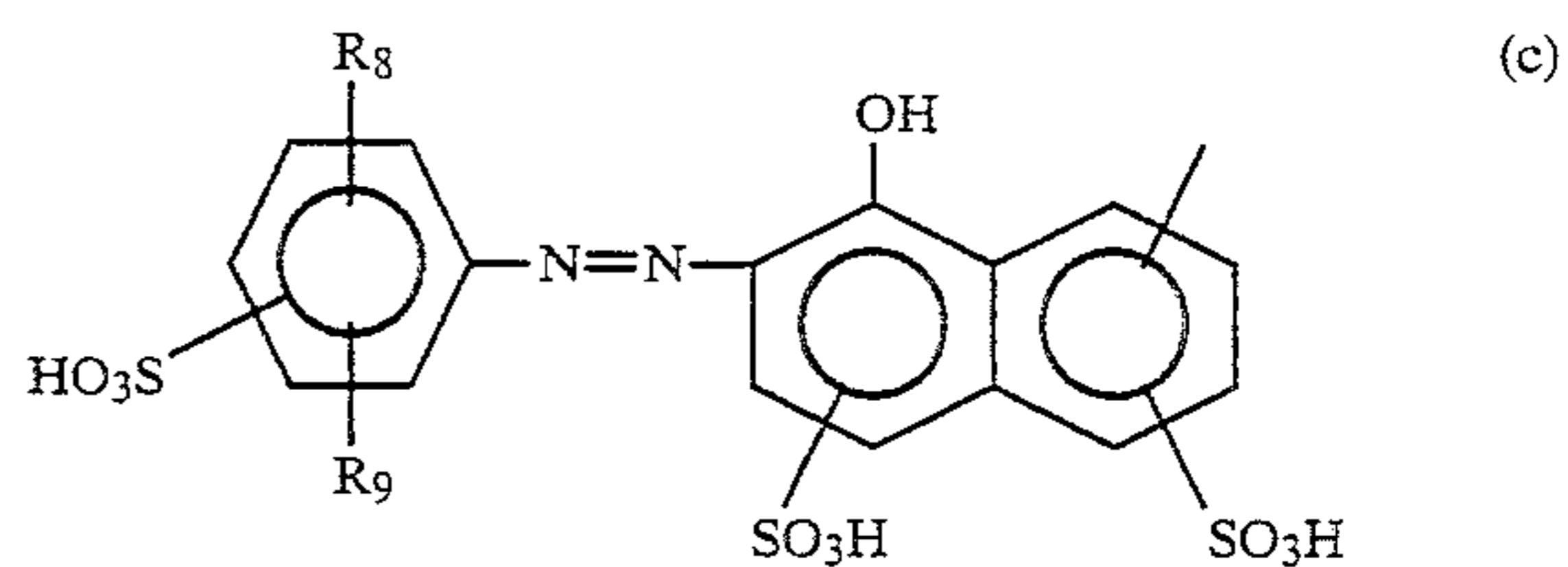
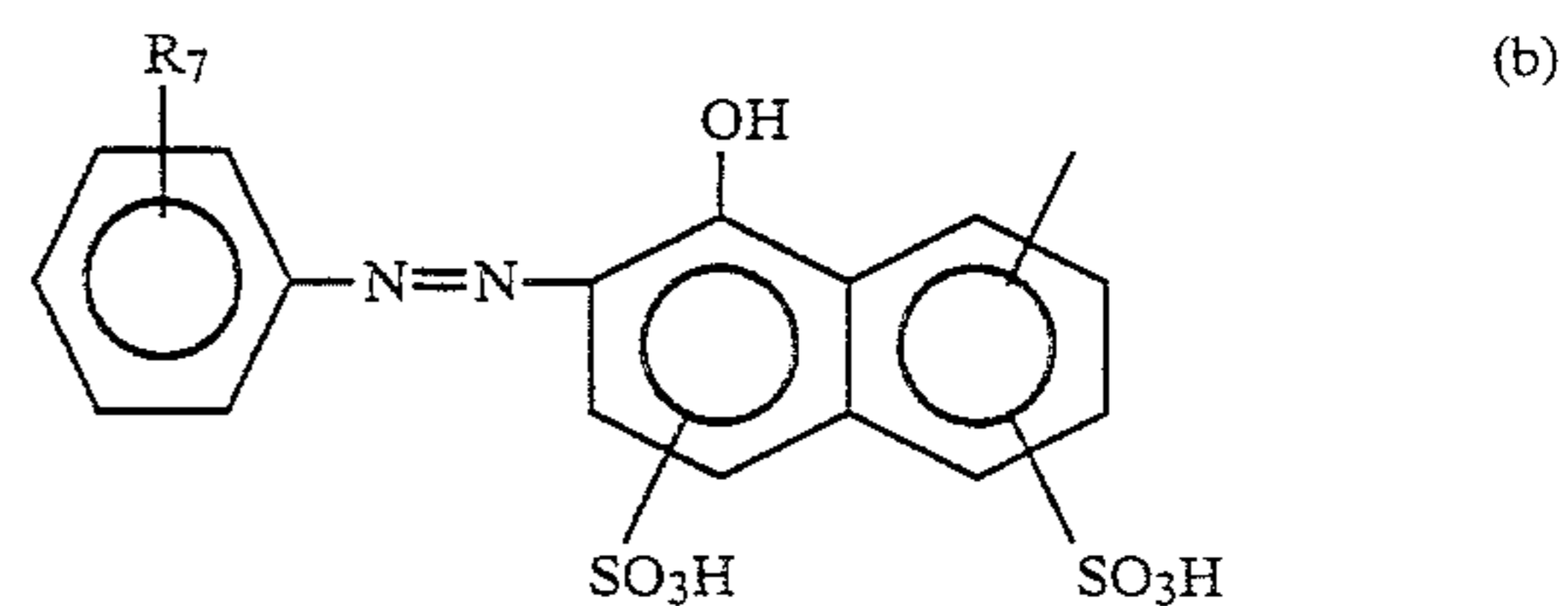
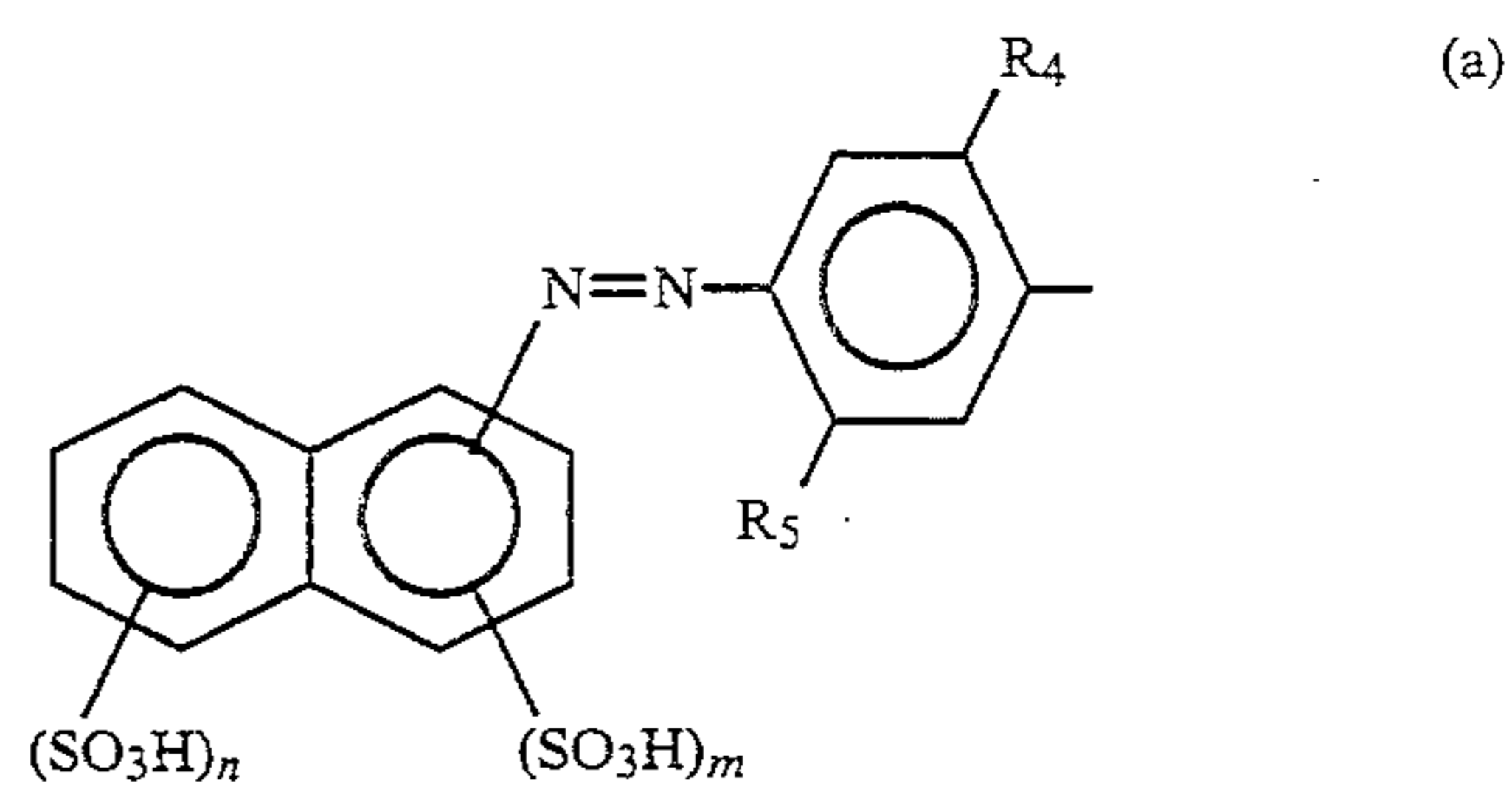


or is a C₂₋₁₀ straight or branched chain alkylene radical,

R_a is hydrogen or C₁₋₄alkyl, and each Hal is fluorine, chlorine or bromine, which compounds are in free acid or salt form, and mixtures thereof.

Examples of residues of monoazo dyestuffs are those which contain components of the aromatic carbocyclic series and heterocyclic series, such as the naphthalene, benzene, pyrazolone and pyridone series. Preferred dyestuff residues are of the formulae Np—N= 60 N—Ar—, Np—N=N—Np—, Ar—N=N—Np— and Het—N=N—Ar—, wherein Np is a radical of the naphthalene series, Ar is a radical of the benzene series and Het is a radical of the heterocyclic series and such residues contain 2 to 4 sulfo groups.

More preferred residues are those of formulae (a), (b), (c), (d), (e), (f) and (g)



in which

R₄ is hydrogen, C₁₋₄alkyl or C₁₋₄alkoxy,
 R₅ is hydrogen, C₁₋₄alkyl, C₁₋₄alkoxy or —NHCOR₆
 where R₆ is C₁₋₄alkyl, —NH₂, —NHC₁₋₄alkyl or
 —N(C₁₋₄alkyl)₂,

R₇ is hydrogen or C₁₋₄alkyl,

R₈ is hydrogen or C₁₋₄alkyl,

R₉ is hydrogen or sulpho,

R₁₀ is hydrogen, C₁₋₄alkyl, carboxy, phenyl or sulphomethyl,

R₁₁ is hydrogen, carboxy, sulpho, sulphomethyl or —CONH₂, with the proviso that when R₁₀ is sulphomethyl, R₁₁ is other than sulpho and sulphomethyl,

R₁₂ is hydrogen, C₁₋₄alkyl or phenyl,

R₁₃ is hydrogen or sulpho,

with the proviso that radical (e) contains at least two sulpho groups,

R₁₄ is C₁₋₄alkyl or carboxy,

each of R₁₅ and R₁₆, independently, is hydrogen C₁₋₄alkyl, chlorine or bromine,

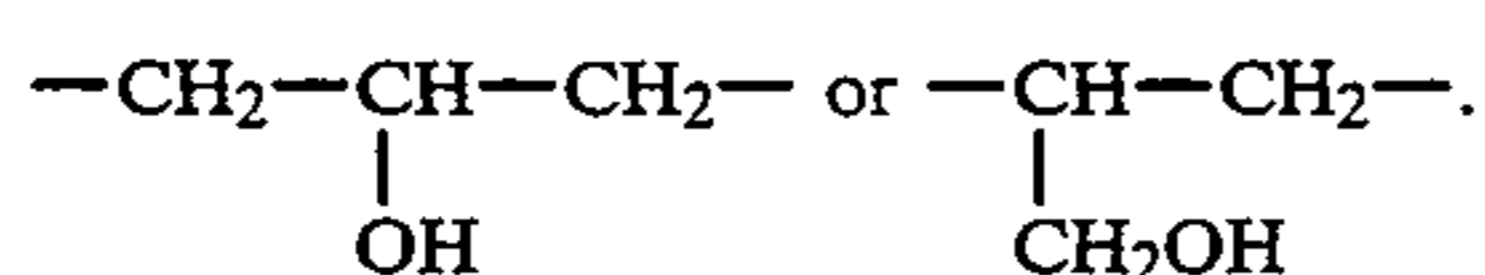
each of m and m' is independently 0 or 1,

each of n and n' is independently 1 or 2, with the provisos that the sum of m+n is 2 or 3 and the sum of m' and n' is 2, and

p is 2.

The hydroxy-substituted alkylene bridge as X preferably contains 3 to 6 carbon atoms and is preferably monohydroxy-substituted. When such alkylene as X contains hetero linkages such as —O— or —N(C₁₋₄alkyl)—, such hetero linkages are separated from the —NR₂— and —NR₃—groups, the hydroxy groups and from each other by at least two carbon atoms. The unsubstituted alkylene bridge as X preferably contains 2 to 6 carbon atoms, most preferably 3 carbon atoms.

X is preferably X' where X' is straight chain or branched chain C₂₋₆alkylene or a monohydroxy-substituted straight or branched chain C₃₋₆alkylene. When X is a monohydroxy-substituted alkylene radical, it is preferably X'', where X'' is a monohydroxy-substituted straight or branched chain C₃₋₆alkylene and more preferably, X''', where X''' is



Most preferably, X is —CH₂CH₂—.

Hal is preferably fluorine or chlorine, more preferably chlorine.

Any alkyl as R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₁₀, R₁₂, R₁₄, R₁₅ and R₁₆ preferably contains 1 or 2 carbon atoms.

Any alkoxy as R₄ or R₅ preferably contains 1 or 2 carbon atoms and is especially methoxy.

Each R₁, independently, is preferably R₁', where R₁' is hydrogen, methyl or ethyl; more preferably R₁ is R₁'', where R₁'' is hydrogen or methyl, with hydrogen being especially preferred.

Each of R₂ and R₃ is preferably R₂' and R₃', where each of R₂' and R₃', independently, is hydrogen, methyl, ethyl or hydroxyethyl. More preferably R₂ and R₃ are R₂'' and R₃'', where each of R₂'' and R₃'', independently, is hydrogen or methyl, with hydrogen being most preferred.

R₄ is preferably R₄', where R₄' is hydrogen methyl or methoxy.

R₅ is preferably R₅', where R₅' is hydrogen methyl or —NHCOR₆', where R₆' is methyl, ethyl, —NH₂, —NHC₁₋₂alkyl or —N(C₁₋₂alkyl)₂. More preferably R₅

is R₅'', where R₅'' is hydrogen, methyl or —NHCOR₆'', where R₆'' is methyl, ethyl or —NH₂, especially methyl or —NH₂.

When R₅ is —NHCOR₆, R₄ is preferably hydrogen, and when R₅ is C₁₋₄alkyl, especially methyl, R₄ is preferably hydrogen or methoxy. When R₅ is hydrogen, R₄ is preferably hydrogen.

R₇ is preferably hydrogen.

R₈ is preferably R₈', where R₈' is hydrogen, methyl or ethyl.

R₁₀ is preferably R₁₀', where R₁₀' is hydrogen or C₁₋₂alkyl, with methyl being most preferred.

R₁₁ is preferably R₁₁' where R₁₁' is hydrogen, sulphomethyl or —CONH₂.

R₁₂ is preferably R₁₂', where R₁₂' is hydrogen or C₁₋₂alkyl, with ethyl being especially preferred.

R₁₃ is preferably hydrogen when R₁₁ is sulphomethyl and is sulpho when R₁₀ is R₁₀' and R₁₁ is hydrogen or —CONH₂.

R₁₄ is preferably R₁₄', where R₁₄' is methyl or carboxy with carboxy being most preferred.

R₁₅ and R₁₆ are preferably R₁₅' and R₁₆', where each of R₁₅' and R₁₆', independently, is hydrogen, methyl or chlorine

p is preferably 1.

In the residues of formula (a) the azo group is bound to the 1- or 2-position, preferably the 2-position.

In the radicals of formula (a) when the azo group is bound to the 2-position and when n is 2 and m is 1 the sulpho groups are in the 3,6,8-, 4,6,8-, 1,5,7- or 3,5,7-positions, preferably in the 3,6,8- or 4,6,8-positions. When the azo group is in the 1-position the sulpho groups are preferably in the 2,5,7- or 3,6,8-positions.

In the radicals of formula (a) when n is 1 and m is 1 the azo group is preferably in the 2-position, and the sulpho groups are preferably in the 1,5-, 1,6- or 4,8-positions, and when n is 2 and m is 0 they are preferably in the 6,8-positions.

In the radicals of formula (d) each of m' and n' is preferably 1; more preferably, the azo group is in the 2-position, and the sulpho groups are in the 1,5- or 1,6-positions.

In the radicals of formulae (b), (c) and (d) the sulpho groups on the hydroxynaphthalene group are preferably in the 3- and 6-positions.

In the radical of formula (g), preferably the azo group is in the 2-position and the sulpho group in the 1-position.

In the radicals of formula (c), preferably one of R₈, R₉ and the sulpho group is in the 2-position; more preferably the sulpho group is in the 2-position.

Preferably only one of D and D' signifies a residue containing a heterocyclic group.

Preferred compounds of formula I are those

(i) in which D is a radical of formula (a) in which m is 1 and n is 1 or 2 or m is 0 and n is 2, R₄ is hydrogen and R₅ is —NHCOR₆, Hal is chlorine, R₂ and R₃ are R₂' and R₃' and D' is a radical of formula (a) in which m is 1 and n is 1 or 2, R₄ is R₄', R₅ is R₅' other than —NHCOR₆, and X is X', preferably X'';

(ii) in which D is a radical of formula (a) in which m is 1 and n is 2, R₂ and R₃ are R₂' and R₃', R₄ is hydrogen and R₅ is —NHCOR₆, Hal is chlorine and D' is a radical of formula (a) in which m is 1 and n is 1 and R₄ is R₄', R₅ is R₅', and X is X', preferably X'';

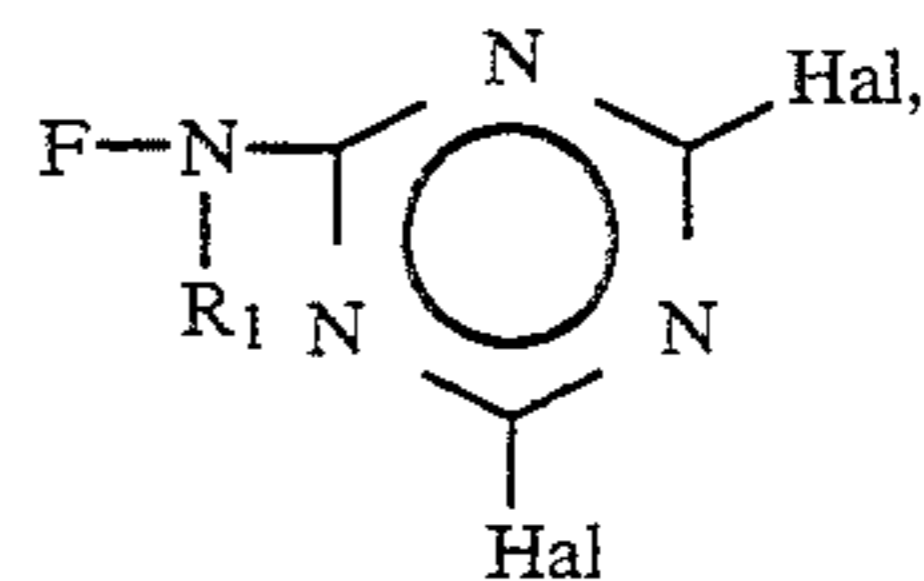
(iii) in which D is a radical of formula (a) in which m is 1 and n is 2, R₂ and R₃ are R₂' and R₃', R₄ is R₄' and

- R₅ is R₅' , Hal is chlorine, D' is a radical of formula (b) or (c) in which R₇ is hydrogen and R₈ is R₈' , and X is X' preferably X'';
- (iv) those in which D is a radical of formula (a) in which m is 1 and n is 1 or 2 or, m is 0 and n is 2, R₂ and R₃ are R₂' and R₃' , R₄ is R₄' and R₅ is R₅' , Hal is chlorine and D' is a radical of formula (b) or (c) in which R₇ is hydrogen and R₈ is R₈' , and X is X' preferably X'';
- (v) those in which D is a radical of formula (d) in which each of m' and n' is 1, R₂ and R₃ are R₂' and R₃' , D' is a radical of formula (a) in which n is 1 and m is 1 or n is 2 and m is 0, preferably the latter, R₄ is hydrogen and R₅ is —NHCOR₆, Hal is chlorine, and X is X', preferably X'';
- (vi) those in which D is a radical of formula (e) in which R₁₀ is R₁₀' , R₁₁ is R₁₁' and R₁₂ is R₁₂' , R₂ and R₃ are R₂' and R₃' , D' is a radical of formula (b) or (c), in which R₇ is hydrogen and R₈ is R₈' , Hal is chlorine, and X is X' preferably X'';
- (vii) those in which D is a radical of formula (f) in which R₁₄ is R₁₄' and R₁₅ is R₁₅' , R₁₆ is R₁₆' and p is 1 R₂ and R₃ are R₂' and R₃' and D' is a radical of formula (b) or (c), in which R₇ is hydrogen and R₈ is R₈' Hal is chlorine, and X is X' preferably X'';
- (viii) those in which D is a radical of formula (g), R₂ and R₃ are R₂' and R₃' , D' is a radical of formula (d) in which each of m' and n' is 1 or of formula (c) in which R₈ is R₈' , Hal is chlorine and X is X' ;
- (ix) those in which D is a radical of formula (c) in which R₈ and R₉ are hydrogen, R₂ and R₃ are R₂' and R₃' , D' is a radical of formula (d) in which each of m' and n' is 1, Hal is chlorine, and X is X' ;
- (x) those of (i) to (ix) in which X is X''' ;
- (xi) those of (i) to (ix) in which X is —CH₂CH₂— ;
- (xii) those of (i) to (xi) in which R₁, R₂ and R₃ are hydrogen;
- (xiii) those wherein D and D' are different groups of formulae (a), (b), (c), (d), (e), (f) and (g);
- (xiv) those of (xiii) wherein X is X' ;
- (xv) those of (xiv) wherein X is X'' ;
- (xvi) those of (xiv) wherein X is linear or branched C₂₋₆-alkylene;
- (xvii) those of (xiii) wherein R₂ is R₂' , and R₃ is R₃' ;
- (xviii) those of (xiii) wherein R₄ is R₄' , and R₅ is R₅' ;
- (xix) those of (xiii) wherein R₄ is hydrogen when R₅ is hydrogen or —NHCOR₆ and is hydrogen or methoxy when R₅ is C₁₋₄alkyl;
- (xx) those of (xiii) wherein R₇ is hydrogen and R₈ is R₈' ;
- (xxi) those of (xiii) wherein R₁₀ is R₁₀' , R₁₁ is R₁₁' , R₁₃ is hydrogen or sulfo, with the proviso that R₁₃ is hydrogen when R₁₁ is sulfomethyl and is sulfo when R₁₁ is hydrogen or —CONH₂ R₁₄ is R₁₄' , R₁₅ is R₁₅' , R₁₆ is R₁₆' and p is 1;
- (xxii) those of (xiii) wherein R₁, R₂ and R₃ are hydrogen; and
- (xxiii) those of (xxii) wherein each Hal is chloro.

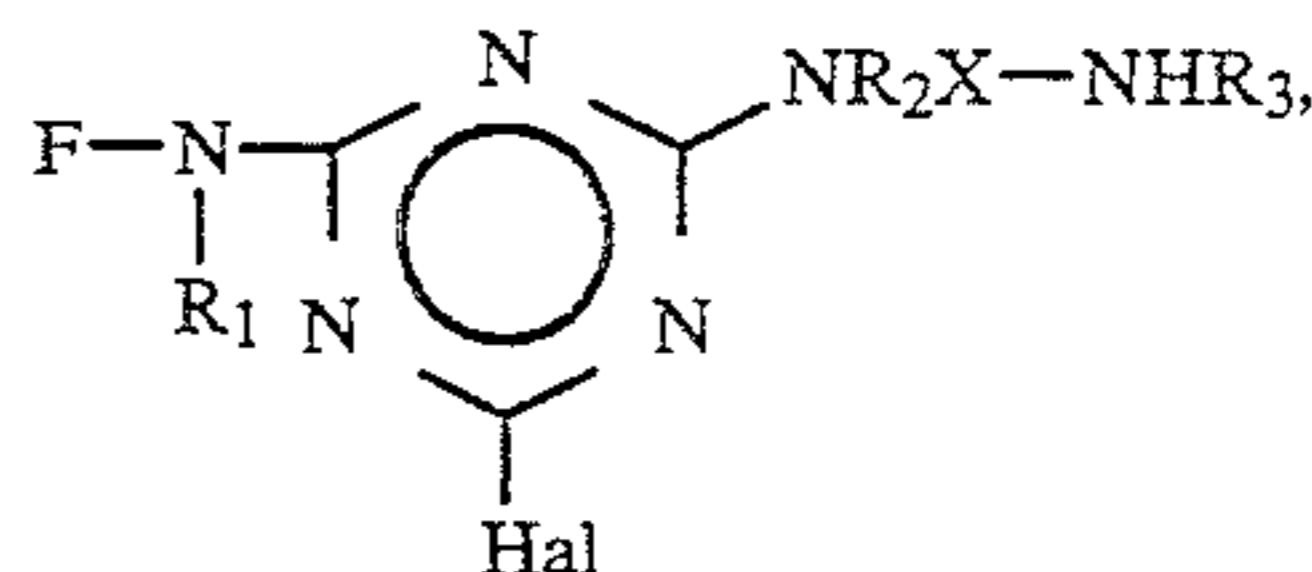
The cations of the sulpho groups when the compounds of formula I are in salt form may be any of those non-chromophoric cations common in the chemistry of reactive dyestuffs. Examples of suitable cations are alkali metal cations and substituted or unsubstituted ammonium, such as sodium, lithium, potassium, ammonium, mono-, di- and tetramethylammonium, triethylammonium and mono-, di- and triethanolammonium.

The present invention further provides a process for the production of compounds of formula I, as defined

above, comprising condensing a compound of formula II



in which F is D or D', with a compound of formula III



in which F₁ is D' when F is D or is D when F' is D'.

The reaction is carried out in accordance with known methods. Suitably the reaction is effected in a neutral to alkaline medium in the presence of an acid binding agent. The reaction temperature is preferably in the range of 30° to 60° C.

The compounds of formulae II and III may be prepared in accordance with known methods. The compounds of formula III are preferably prepared by reacting the dyestuff F₁—NHR₁ with 2,4,6-trihalo-1,3,5-triazine, optionally in the presence of an acid binding agent, at 0°–5° C. in a weakly acid medium, i.e. pH 4–6.5, and then reacting the product with HNR₂—X—NR₃H. The second reaction is suitably carried out from room temperature to 50° C. in a neutral medium advantageously in the presence of an acid binding agent.

The compounds of formula I and mixtures thereof are useful as reactive dyestuffs for dyeing or printing hydroxy-group nitrogen-containing organic substrates. Preferred substrates are leather and textiles comprising or consisting of natural or synthetic polyamides such as wool, silk and nylon, natural or regenerated cellulose such as cotton, viscose and spun rayon. When Hal is chlorine dyeing may be effected equally well at 80° C. as at 100° C. When Hal is fluorine the dyestuffs are so called cold dyes, i.e., dyeing is preferably effected at temperatures in the range of between 30° and 50° C.

Dyeing is effected in accordance with known methods. Preferably, dyeing is effected by the exhaust method. Furthermore, dyeing may also be carried out using the Pad-Batch process.

The dyeings and prints obtained have good fastness properties, especially good light and wet fastnesses such as wash, water, sea water and sweat fastness. They show notable resistance to hydrolysis in the presence of perborate. Furthermore, the dyeings and prints are stable to any oxidative influences, e.g., stable to chlorinated water, hypochlorite- or peroxide-bleach or perborate containing wash liquors. The compounds according to the invention have good water-solubility in the presence of salt, they are only very slightly affected by salts. They migrate well and give even, unmottled dyeings. In view of their good build-up power the compounds of formula I give high exhaust and fixation yields. The portion of unfixed dye can be easily washed off the substrate.

The compounds of formula I are well compatible with other reactive dyes. They may be applied per se or

in combination with appropriate fibre-reactive dyes of the same class having analogous dyeing properties such as common fastness properties, extent of ability to exhaust from the dyebath onto the fibre, etc. The dyeings obtained with such combination mixtures have good fastness properties and are comparable to those obtained with a single dye.

The following examples further serve to illustrate the invention. In the examples all parts and percentages are by weight or volume, and the temperatures are in degrees Centigrade.

EXAMPLE 1

191.5 Parts 2-aminonaphthalene-3,6,8-trisulphonic acid are suspended in 500 parts water. After the addition of 125 parts 30% hydrochloric acid with the addition of ice to cool to 0° to 6°, diazotization is carried out over a period of 45 minutes with 125 parts 4N sodium nitrite solution. Stirring is effected for 1 hour and any excess nitrite is decomposed with sulphamic acid.

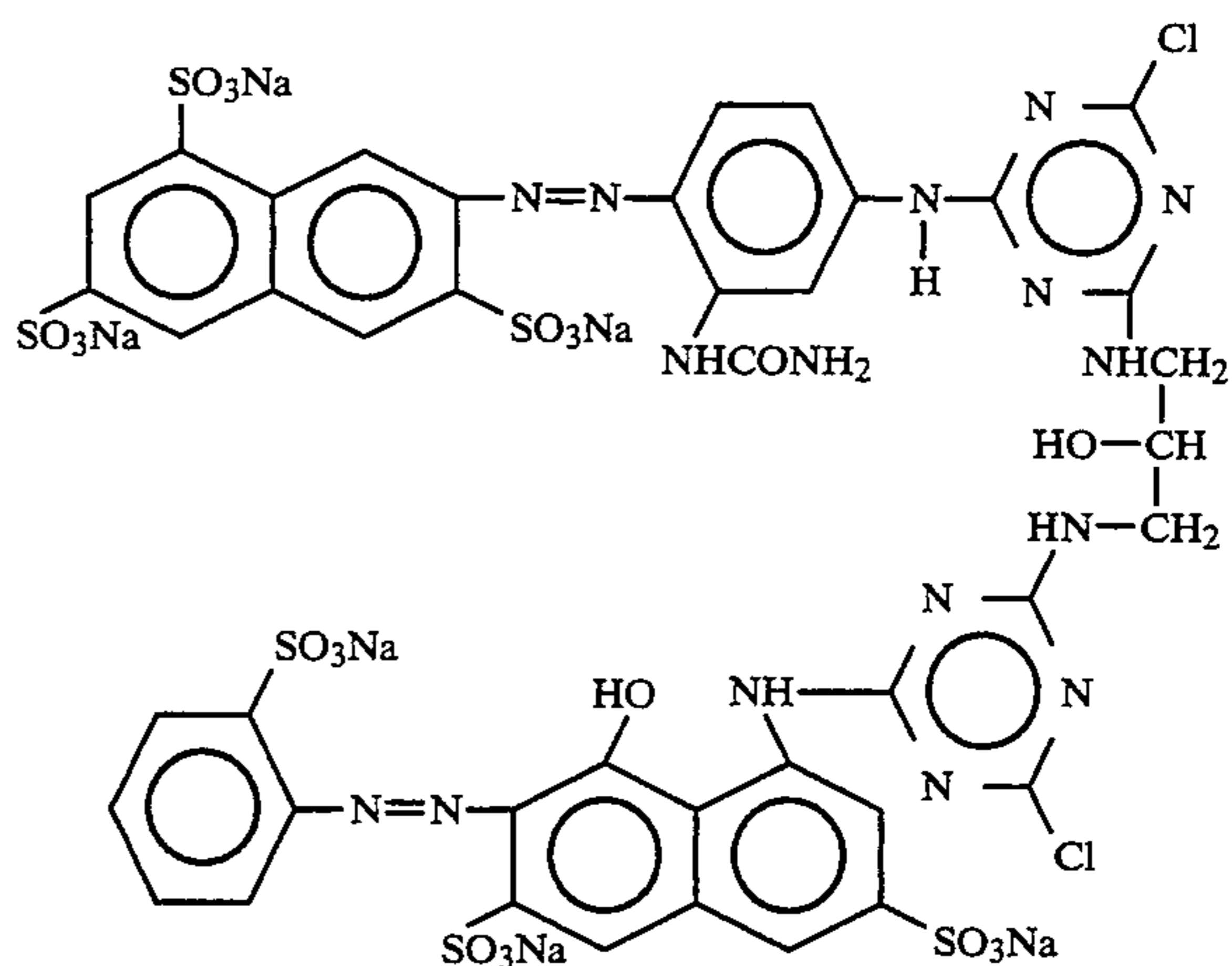
75.5 Parts 1-amino-3-ureidobenzene are dissolved in 250 parts water with the addition of 50 parts 30% hydrochloric acid and cooling to a temperature under 5° with ice. The diazo suspension obtained as described above is slowly added thereto with simultaneous addition of 100 parts sodium acetate (crystalline), portionwise. The solution is stirred overnight and then adjusted to pH 4.5 with a little 20% soda solution and salted out with approximately 10 mol % sodium chloride. The dye is filtered off.

At approximately 2°, 50 parts cyanuric chloride are added to a solution of the dyestuff so obtained in 800 parts water, the pH of the solution being adjusted to 5 to 5.5. Stirring is effected at a temperature not exceeding 5°. Subsequently, 42 parts cyanuric chloride are added, and the pH is adjusted to approximately 5.5 with sodium carbonate solution. After completion of the condensation the reaction mixture is treated with activated charcoal and then filtered clear.

37 Parts 1,3-diaminopropanol-2 in 600 parts water are added to the so-obtained dyestuff solution which is stirred overnight at room temperature, the mixture is adjusted to pH 7 and the whole is stirred at 30°-40° C. for approximately a further 6 hours. The product is salted out with sodium chloride and filtered.

Meanwhile 285 parts of the trisodium salt of 8-amino-1-hydroxy-2-(2'-sulphophenylazo)naphthalene-3,6-disulphonic acid in 800 parts water is reacted with 92 parts cyanuric chloride at 0°-5°. The pH of the solution is adjusted to 4 to 4.5 by the addition of aqueous sodium carbonate solution.

The product obtained thereby is reacted with the condensation product with 1,3-diaminopropanol-2 obtained as described above by stirring at room temperature overnight followed by stirring for approximately 6 hours at a temperature of from 40° to 50° C., the pH having being adjusted to 7. After salting out with sodium chloride, filtering and drying in vacuo at approximately 80°, the dyestuff of the formula

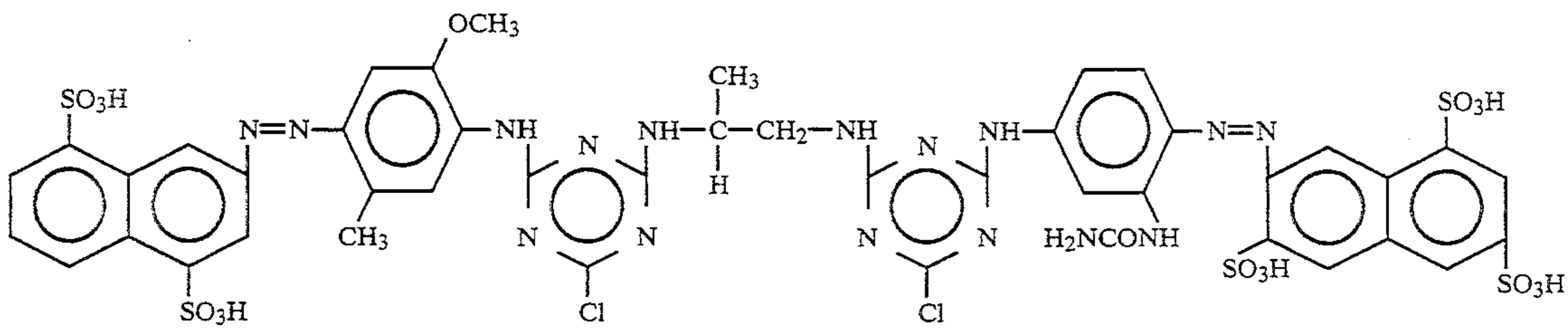


is obtained, which dyes natural and regenerated cellulose in scarlet shades.

EXAMPLE 2

6.9 Parts dichlorotriazine monoazo dyestuff obtained by acid coupling of diazotized 2-aminonaphthalene-3,6,8-trisulphonic acid with m-aminophenylurea and subsequent condensation with cyanuric chloride are dissolved in 70 parts water made neutral and reacted at room temperature with a solution consisting of 0.8 parts 1,2-diaminopropane in 8 parts water and 2 parts 30% hydrochloric acid. The mixture is reacted for 5 hours at a pH of 7 to 8 and a temperature of 25°-35° C. The pH is maintained by the addition of c. 1 part calcined soda dissolved in a little water. After the reaction is ended the completely formed precipitated amino dye is filtered to separate out the by-products. The presscake is stirred into 70 parts water at room temperature and then combined with the aqueous solution of approximately 70 parts by volume containing 5 parts of the dyestuff obtained as follows:

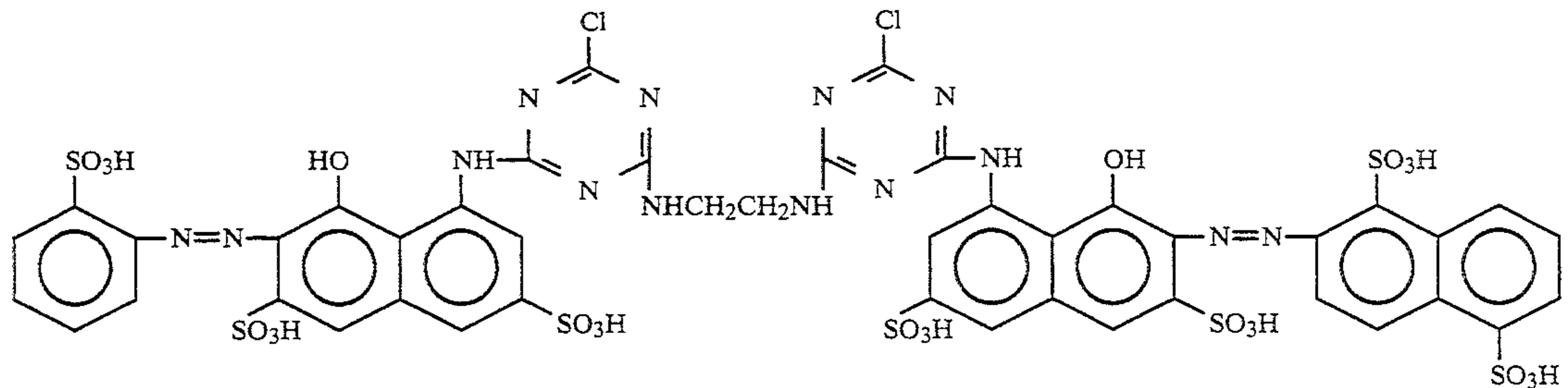
4 Parts of the dye obtained by acid coupling of diazotized 2-aminonaphthalene-4,8-disulphonic acid with 2-amino-1-methoxy-4-methylbenzene are dissolved in 50 parts water and made neutral and then reacted with 1.8 parts cyanuric chloride with vigorous stirring, the pH of approximately 5 at 20° to 25° C. being maintained by the addition of aqueous soda solution. After completion of the reaction the solid colourless impurities are filtered off whereby the solution is ready for use. The connection of the two monoazo dyes is effected over 5 hours at 20° to 30° C. whereby the pH is held at 11 to 11.5 by continuous addition of sodium hydroxide solution. After completion of the reaction in a neutral pH medium the disazo dyestuff is precipitated with the help of sodium chloride and is then filtered. After drying and grinding, an orange powder is obtained which dyes cotton and regenerated cellulose fibres in lively golden-yellow shades. The product, in free acid form, is of the formula



EXAMPLE 3

a) 159.5 Parts of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid in 900 parts of water are reacted at 0-5° with 92 parts of cyanuric chloride whilst maintaining a pH of 3-4 by the addition of aqueous sodium carbonate solution. Within four to five hours, the condensation is completed. The reaction mixture thus obtained is divided into two equal parts, and both parts are further processed separately.

b) 45.4 Parts of 1-aminobenzene-2-sulphonic acid are suspended in 125 parts of water and 150 parts of ice with



the addition of 28.7 parts of a 30% hydrochloric acid while stirring. Diazotization is effected by adding 18.1 parts of sodium nitrite as a 4N aqueous solution during 20 minutes. Any excess nitrite is decomposed with a small amount of sulphamic acid. This cold, yellow diazo suspension is added to the first part of the condensation product obtained under a). Coupling is effected at 5-8° by the addition of a 15% aqueous sodium carbonate solution while stirring. The sodium carbonate solution is added at such a rate as to permit the pH increase to 7 within 45 minutes.

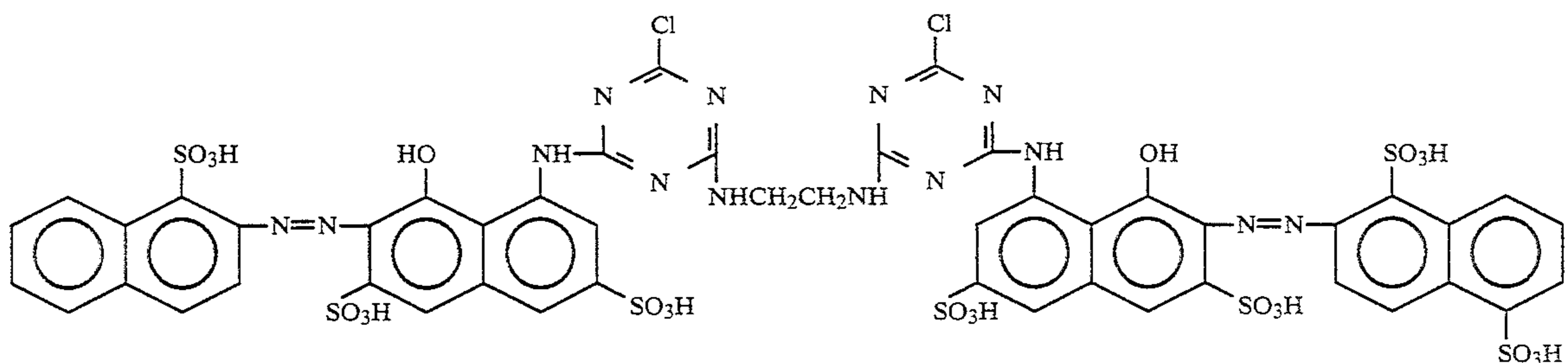
phonic acid and 18.1 parts of sodium nitrite in 34.5 parts of 30% hydrochloric acid. The diazo solution is added to the second part of the condensation product obtained under a). Coupling is effected in analogous manner as described under b). A dark-red suspension is obtained where the dyestuff has precipitated approximately completely.

This suspension is added to the solution of the condensation product obtained under b) with stirring. Condensation is effected at 40° and pH 8 by adding aqueous sodium carbonate solution to obtain the dyestuff of the formula

The dyestuff is isolated by salting out with a mixture of potassium- and sodium-chloride, filtered and dried in vacuo. It is obtained in form of a mixed potassium-/sodium-salt, and dyes natural or regenerated cellulose a brilliant bluish-red shade.

EXAMPLE 4

When in step b) of Example 3, 58.5 parts of 2-aminonaphthalene-1-sulphonic acid are used instead of 45.4 parts of 1-aminobenzene-2-sulphonic acid, the corresponding disazo-dyestuff of the formula



Subsequently, to this coupling mixture a solution prepared from 15 parts of ethylene diamine and 57 parts of 30% hydrochloric acid and 100 parts of ice are added. This reaction mixture is heated to 40°, and the pH is kept at 6.5 by adding aqueous sodium carbonate solution. After one hour, the selective condensation (the reaction of only one amino group of the diamine with one chlorine of the dichlorotriazinyl group) is complete.

c) In the meantime, the second diazo component has been prepared in analogous manner as described under b), using 79.5 parts of 2-aminonaphthalene-1,5-disul-

phonic acid and 18.1 parts of sodium nitrite in 34.5 parts of 30% hydrochloric acid. The diazo solution is added to the second part of the condensation product obtained under a). Coupling is effected in analogous manner as described under b). A dark-red suspension is obtained where the dyestuff has precipitated approximately completely.

This suspension is added to the solution of the condensation product obtained under b) with stirring. Condensation is effected at 40° and pH 8 by adding aqueous sodium carbonate solution to obtain the dyestuff of the formula

The dyestuff is isolated by salting out with a mixture of potassium- and sodium-chloride, filtered and dried in vacuo. It is obtained in form of a mixed potassium-/sodium-salt, and dyes natural or regenerated cellulose a brilliant bluish-red shade.

In analogy with the method described in Examples 1 to 4 further dyestuffs, given in the following Table, may be prepared. The dyestuffs are obtained in the sodium- and mixed sodium-/potassium-salt form, respectively. However, they may be converted to other salt forms in accordance with known methods. In Examples 5 to 21, R₂ and R₃ are hydrogen. In Examples 22 to 54, Hal is chlorine. In the last column DS of the Table the dye shade on cellulose is given, where a is golden-yellow, b is scarlet, c is reddish-yellow, and d is bluish-red.

TABLE

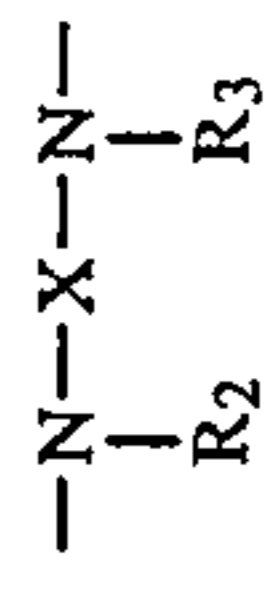
Ex. No.	D-NR ₁	Hal	D'-NR ₁	X	DS
5		Cl		-CH ₂ -CH(OH)-CH ₂ -	a
6	"	"		"	a
7		"		"	b
8		"		"	b
9		"		"	b

TABLE-continued

10		"	"	b
11		Cl		b
12		"		a
13	"	F	"	a
14	"	"		$\text{--CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{--}$
15	"	"		$\begin{matrix} \text{CH}_2\text{OH} \\ \\ \text{--CH--CH}_2\text{--} \end{matrix}$
16		"		a
17		"		b

TABLE-continued

18		Cl		$\text{---CH}_2\text{CHCH}_2\text{---}$ $\quad \quad $ $\quad \quad \text{OH}$	b
19		Cl		"	b
20		Cl	"	"	b
21		Cl	"	"	b



Ex. No.

D---NR₁---

D'---NR₁---

DS

TABLE-continued

22			$\begin{array}{c} \text{CH}_3 \\ \\ \text{---NH---CH---CH}_2\text{---NH---} \end{array}$	a
23	"		"	a
24			$\text{---NH---CH}_2\text{CH}_2\text{CH}_2\text{---NH---}$	a
25	"	"	$\text{---NHCH}_2\text{CH}_2\text{NH---}$	a
26	"	"	$\begin{array}{c} \text{---N---CH}_2\text{CH}_2\text{---NH---} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	a
27		"	$\begin{array}{c} \text{---NH---CH}_2\text{---CH---CH}_2\text{NH---} \\ \\ \text{OH} \end{array}$	a

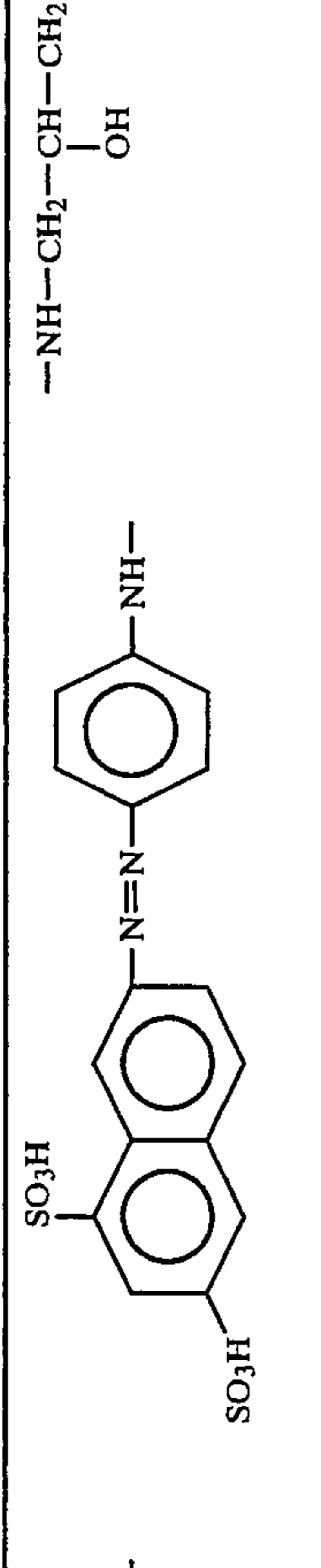
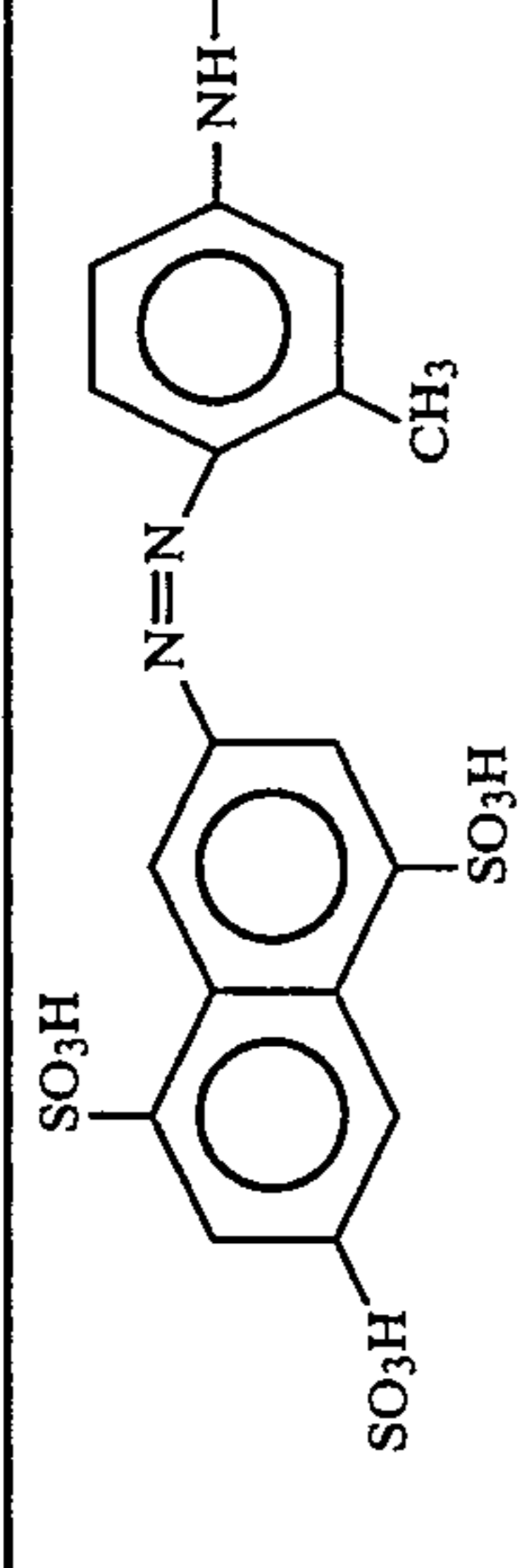




TABLE-continued

28		$\text{--NH--CH}_2\text{--CH(OH)--CH}_2\text{--NH--}$	b
29		"	b
30		"	b
31		"	b
32		"	b

TABLE-continued

33		$\text{--HN--(CH}_2\text{)}_6\text{--NH--}$	b
34	"	"	b
35		$\text{--NH--CH}_2\text{--CH(OH)--CH}_2\text{--NH--}$	c
36	"	"	c
37	"	"	c
38	"	"	c

TABLE-continued

39			c
40	"	"	c
41	"		c
42	"	"	c
43			d
44	"		d

$$\text{--NH--CH}_2\text{--CH(OH)--CH}_2\text{--NH--}$$

TABLE-continued

Ex. No.	D-NR ₁ -	D'-NR ₁ -	-NR ₂ -X-NR ₃ -	DS
45			$\text{--NH--CH}_2\text{CH}_2\text{--N--CH}_2\text{CH}_2\text{OH}$	d
46	"		$\text{--NHCH}_2\text{CH}_2\text{CH}_2\text{NH--}$	d
47	"	"	$\text{--NH--CH(CH}_3\text{)--CH}_2\text{--NH--}$	d
48	"	"	$\text{--N(CH}_3\text{)--CH}_2\text{CH}_2\text{CH}_2\text{--NH--}$	d
49	"	"	$\text{--NH--CH}_2\text{CH}_2\text{N(CH}_2\text{CH}_2\text{OH)--}$	d
50			"	d
51			$\text{--NH--CH}_2\text{CH}_2\text{--N--CH}_2\text{CH}_2\text{OH}$	d

TABLE-continued

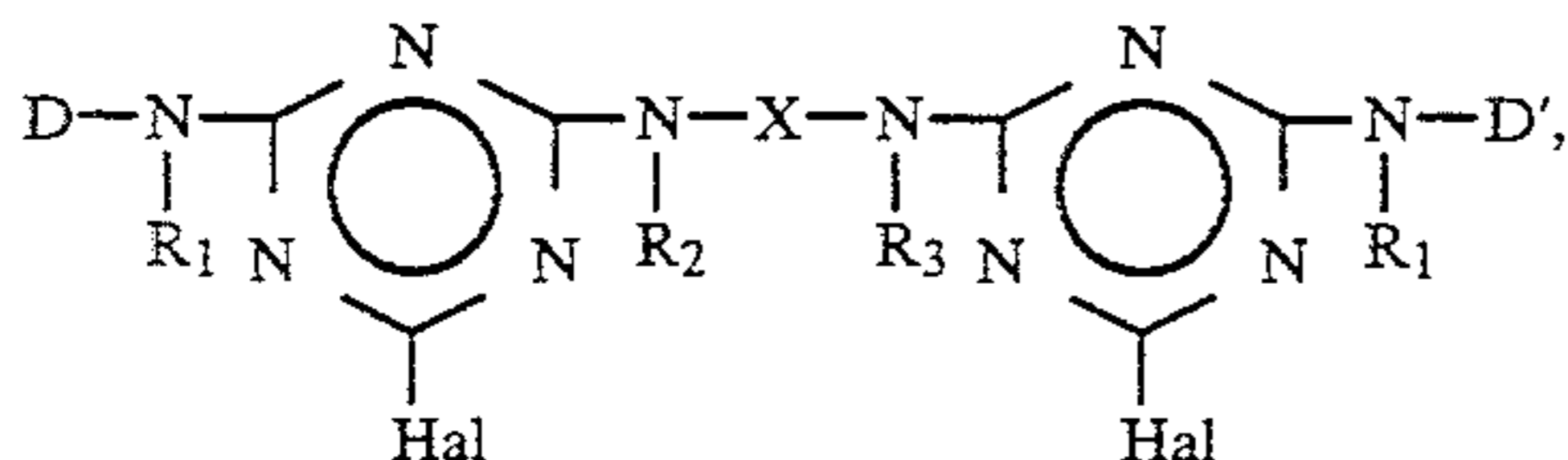
52	"		"	d	
53	"			-NH(CH2)4NH-	d
54	"			-NHCH2CHNH- CH3	a

APPLICATION EXAMPLE

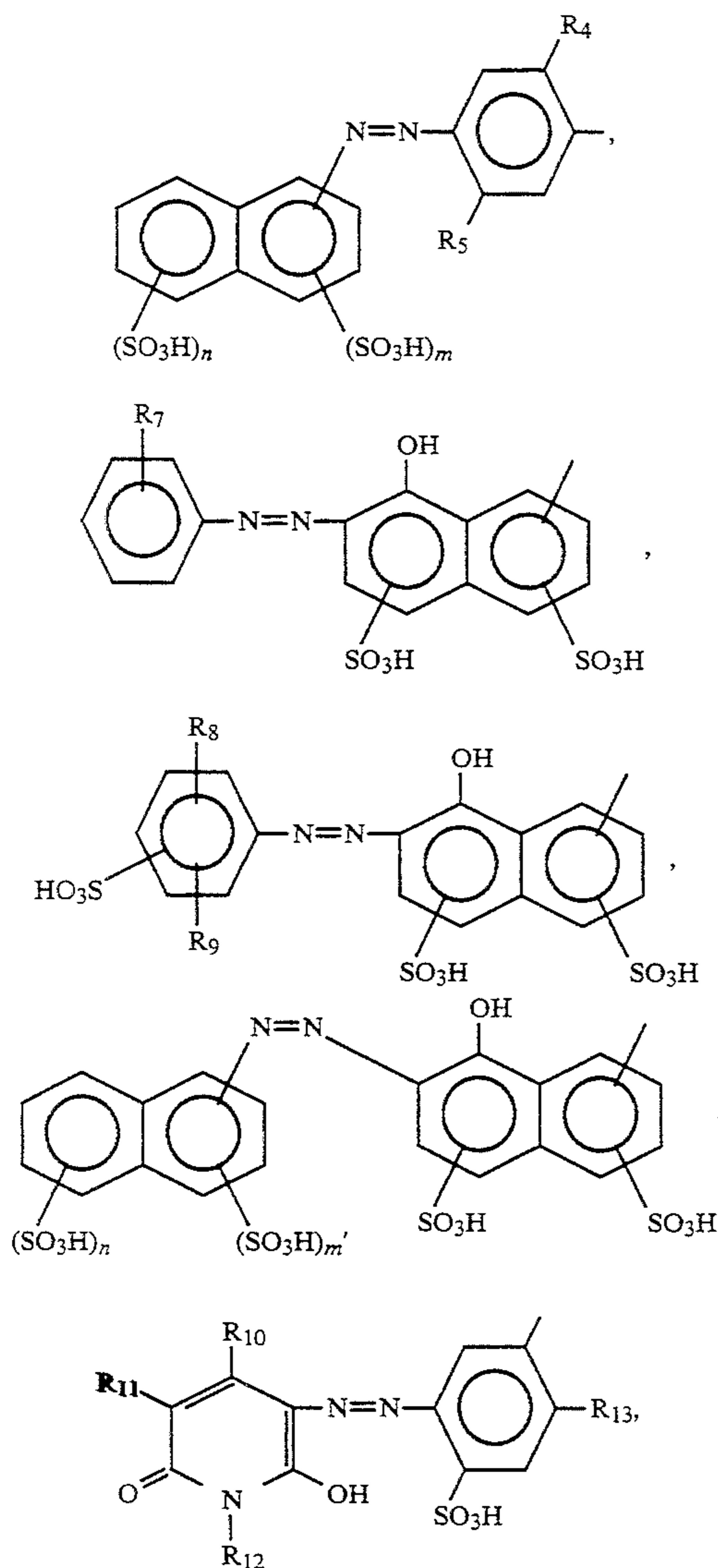
1 Part of the dye of Example 1 is dissolved in 300 parts water, 10 parts cotton are added to the dyebath and the temperature is raised to 80° in 10 minutes. 15 parts Glauber salts are added and, 30 minutes thereafter, 3 parts sodium carbonate. Dyeing is continued for 1 hour. Subsequently, the dyed material is rinsed cold and then hot. The dyeing is soaped at the boil for 20 minutes in 500 parts water and 0.5 parts sodium alkylsulphonate. After rinsing a scarlet dyeing with good light-, wet-, and chlorine-fastness is obtained.

What is claimed is:

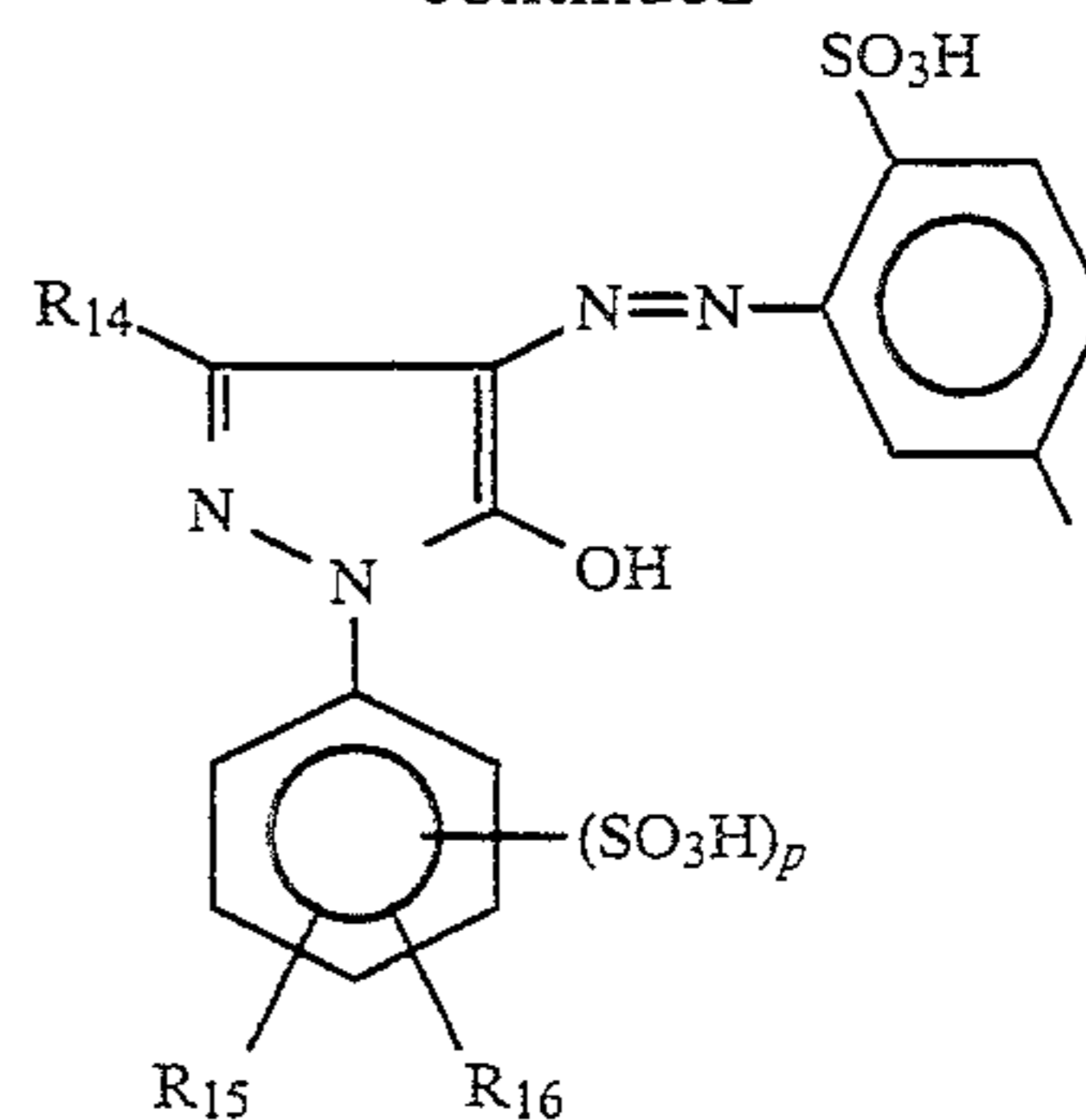
1. A compound of the formula



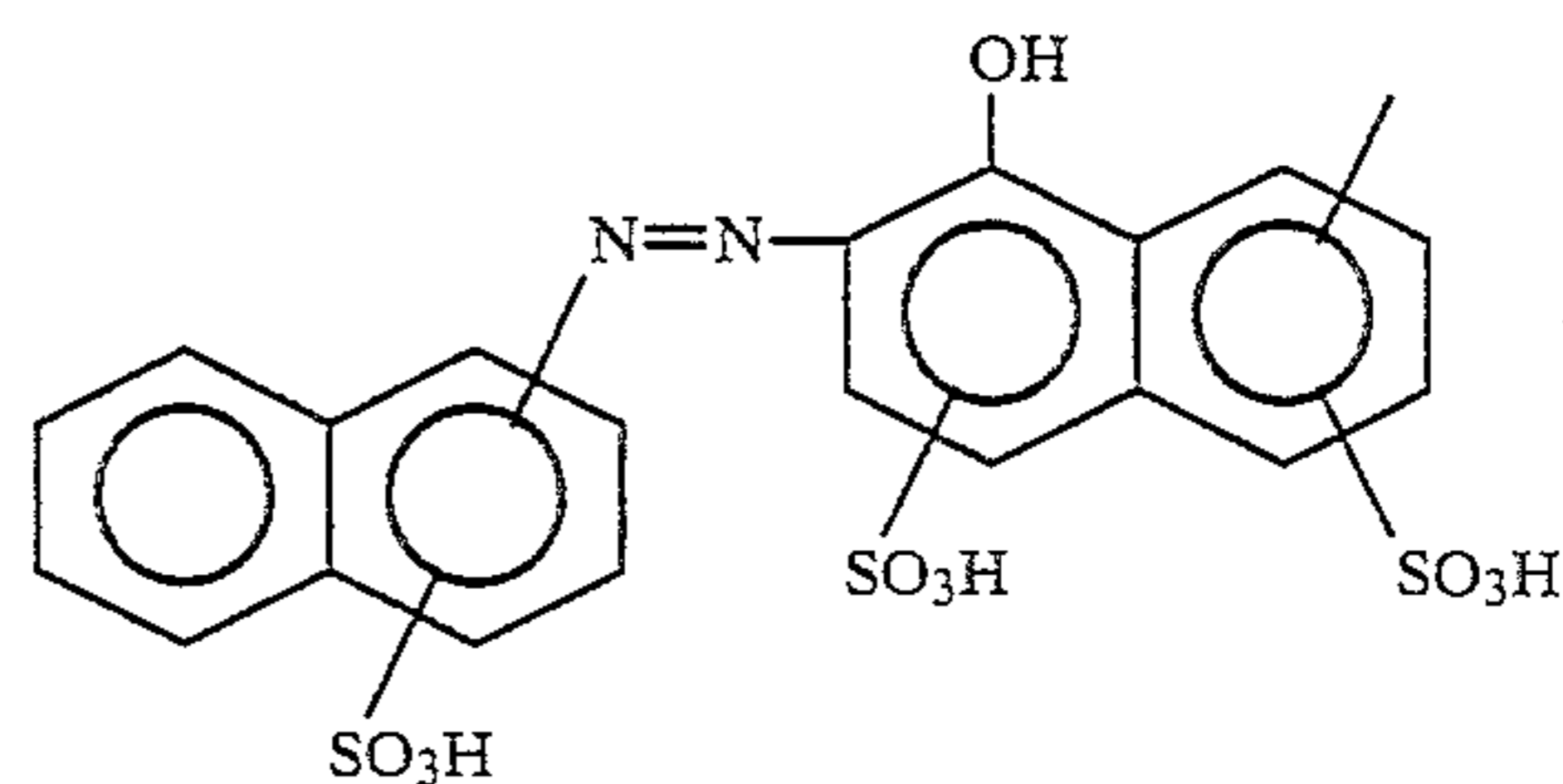
or a salt thereof each cation of which is non-chromophoric, or a mixture of such compounds or salts, wherein each of D and D' is independently



-continued



15 or



25

wherein

R₄ is hydrogen, C₁₋₄alkyl or C₁₋₄alkoxy,

R₅ is hydrogen, C₁₋₄alkyl, C₁₋₄alkoxy or -N-H-CO-R₆, wherein R₆ is C₁₋₄alkyl, -NH₂, -NH-C₁₋₄alkyl or -N(C₁₋₄alkyl)₂,

R₇ is hydrogen or C₁₋₄alkyl,

R₈ is hydrogen or C₁₋₄alkyl,

R₉ is hydrogen or sulfo,

R₁₀ is hydrogen, C₁₋₄alkyl, carboxy, phenyl or sulfomethyl,

R₁₁ is hydrogen, carboxy, sulfo, sulfomethyl or carbamoyl,

R₁₂ is hydrogen, C₁₋₄alkyl or phenyl,

R₁₃ is hydrogen or sulfo, with the provisos that at least one of R₁₀, R₁₁ and R₁₃ is sulfo or sulfomethyl and that R₁₁ is hydrogen, carboxy or carbamoyl when R₁₀ is sulfomethyl,

R₁₄ is C₁₋₄alkyl or carboxy,

each of R₁₅ and R₁₆ is independently hydrogen, C₁₋₄alkyl, chloro or bromo,

each of m and m' is independently 0 or 1,

each of n and n' is independently 1 or 2, with the provisos that m+n is 2 or 3, and m'+n' is 2, and p is 1 or 2,

with the proviso that D and D' are different,

each R₁ is independently hydrogen or C₁₋₄alkyl,

each of R₂ and R₃ is independently hydrogen, C₁₋₄alkyl or 2-, 3- or 4-hydroxy(C₂₋₄alkyl),

X is linear or branched C₂₋₁₀alkylene, linear or branched C₃₋₁₀alkylene monosubstituted or disubstituted by hydroxy or linear or branched C₃₋₁₀alkylene monosubstituted or disubstituted by hydroxy and containing 1 or 2 radicals selected from -O- and -NRa-, with the proviso that any -O- or -NRa- radical is separated from any other such radical, each hydroxy group and the -NR₂- and -NR₃- radicals by at least two carbon atoms, wherein Ra is hydrogen or C₁₋₄alkyl, and

60

each Hal is fluoro, chloro or bromo.

2. A compound according to claim 1, or a salt thereof each cation of which is non-chromophoric.

65

3. A compound according to claim 2, or a salt thereof each cation of which is sodium, lithium, potassium, ammonium, methylammonium, dimethylammonium, tetramethylammonium, triethylammonium, ethanolammonium, diethanolammonium or triethanolammonium.

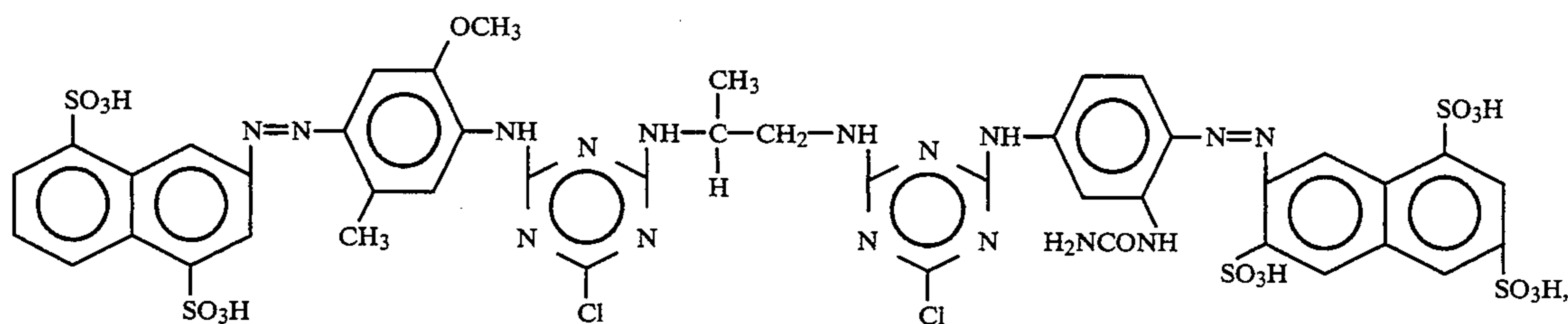
4. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein X is linear or branched C₂₋₁₀alkylene or linear or branched C₃₋₁₀alkylene monosubstituted or disubstituted by hydroxy.

5. A compound according to claim 4, or a salt thereof each cation of which is non-chromophoric, wherein X is linear or branched C₂₋₆alkylene or linear or branched C₃₋₆alkylene monosubstituted by hydroxy.

6. A compound according to claim 5, or a salt thereof each cation of which is non-chromophoric, wherein X is linear or branched C₂₋₆alkylene.

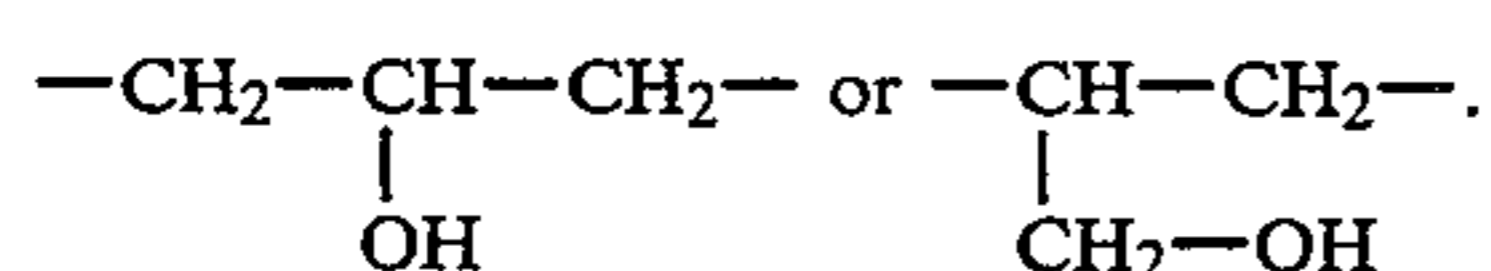
7. A compound according to claim 5, or a salt thereof each cation of which is non-chromophoric, wherein X is linear or branched C₃₋₆alkylene monosubstituted by hydroxy.

8. A compound according to claim 7, or a salt thereof each cation of which is non-chromophoric, wherein X



40

is



9. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein each R₁ is independently hydrogen, methyl or ethyl.

10. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein each of R₂ and R₃ is independently hydrogen, methyl, ethyl or 2-hydroxyethyl.

11. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein

R₄ is hydrogen, methyl or methoxy,

R₅ is hydrogen, methyl or —NH—CO—R₆' , wherein

R₆' is methyl, ethyl, —NH₂, —NH—C₁₋₂alkyl or —N(C₁₋₂alkyl)₂,

R₇ is hydrogen,

R₈ is hydrogen, methyl or ethyl,

R₁₀ is hydrogen or C₁₋₂alkyl,

R₁₁ is hydrogen, sulfomethyl or carbamoyl,

R₁₃ is hydrogen or sulfo, with the proviso that R₁₃ is hydrogen when R₁₁ is sulfomethyl and is sulfo when R₁₁ is hydrogen or carbamoyl,

R₁₄ is methyl or carboxy,

each of R₁₅ and R₁₆ is independently hydrogen, methyl or chloro, and

p is 1.

12. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein R₄ is hydrogen when R₅ is hydrogen or —N—H—CO—R₆ and is hydrogen or methoxy when R₅ is C₁₋₄alkyl.

13. A compound according to claim 2, or a salt thereof each cation of which is non-chromophoric, wherein each

R₁ is hydrogen,

R₂ is hydrogen, and

R₃ is hydrogen.

14. A compound according to claim 13, or a salt thereof each cation of which is non-chromophoric, wherein each Hal is chloro.

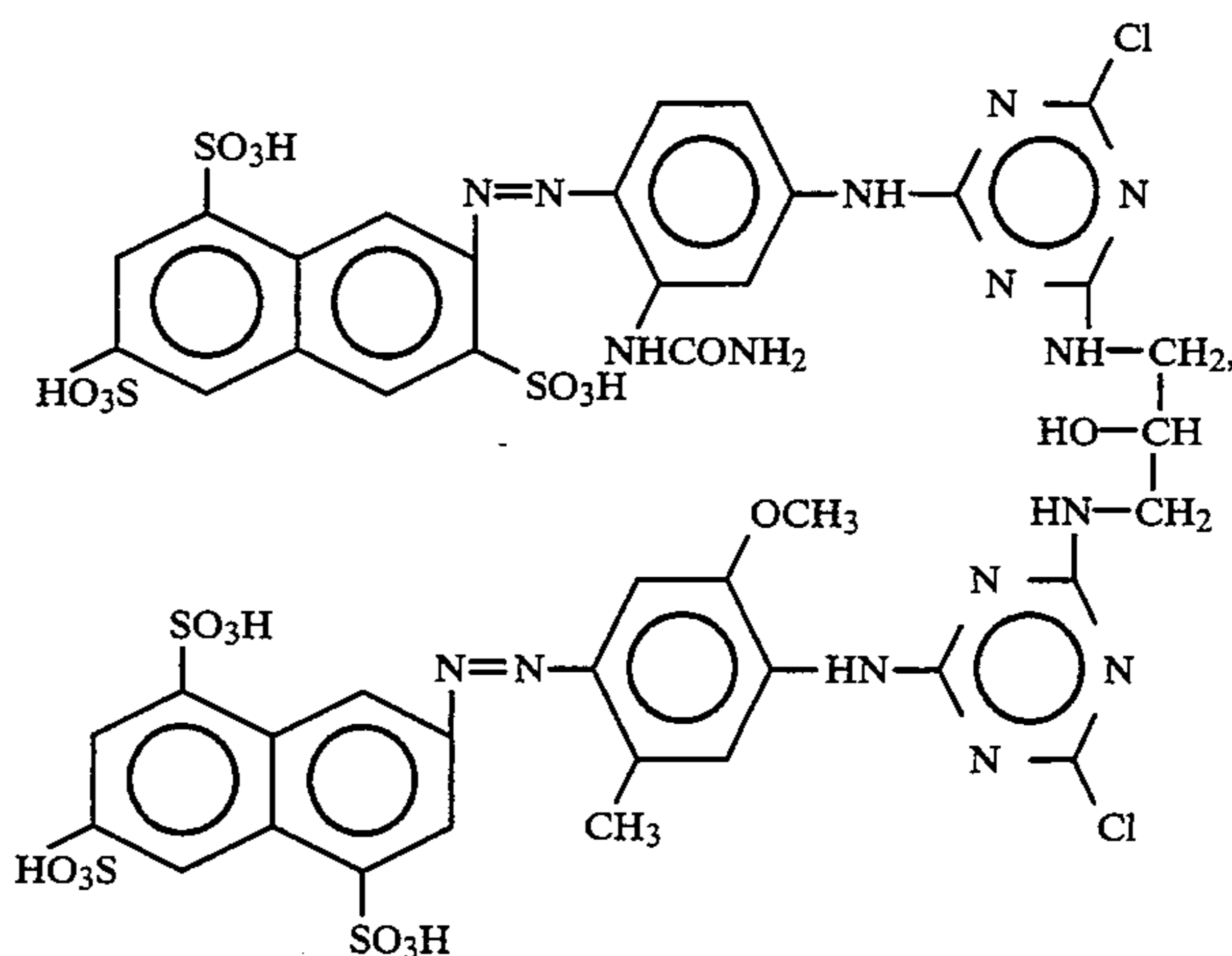
15. A compound according to claim 14, or a salt thereof each cation of which is non-chromophoric, wherein X is linear or branched C₂₋₆alkylene.

16. The compound according to claim 15 having the formula

40

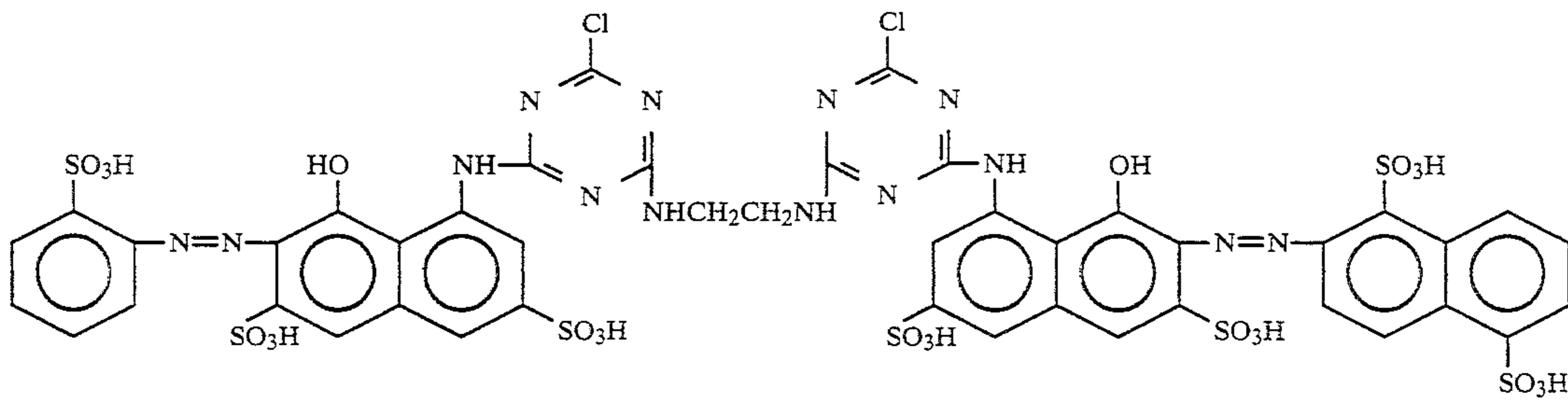
or a salt thereof each cation of which is non-chromophoric.

17. The compound according to claim 14 having the formula



or a salt thereof each cation of which is non-chromophoric.

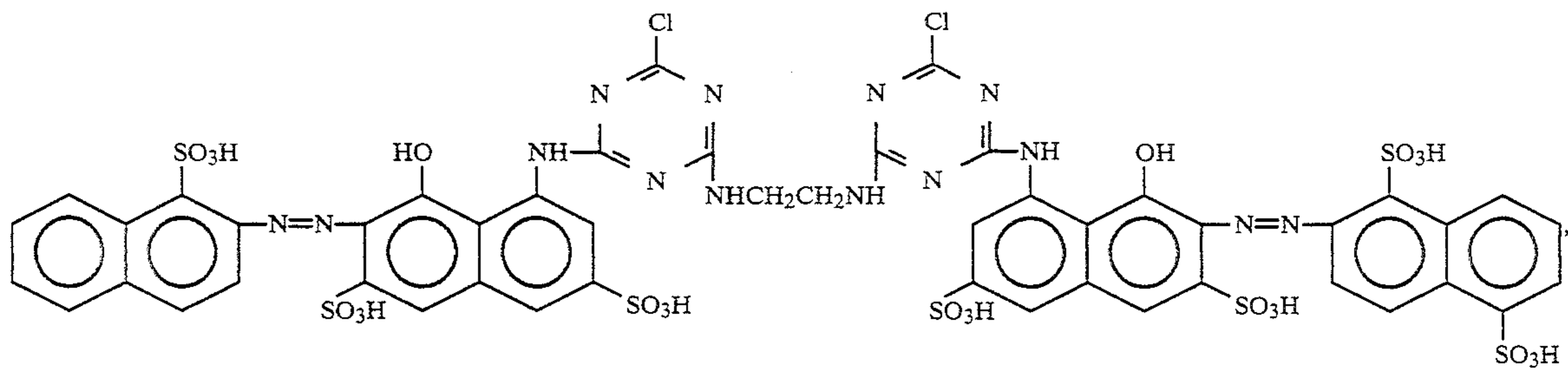
18. The compound according to claim 15 having the formula



or a salt thereof each cation of which is non-chromophoric.

19. The compound according to claim 15 having the formula

15 containing or hydroxy group-containing organic substrate comprising applying to a nitrogen-containing or hydroxy group-containing organic substrate a compound according to claim 1, a salt thereof each cation of which



or a salt thereof each cation of which is non-chromophoric.

20. A process for dyeing or printing a nitrogen-con-

is non-chromophoric or a mixture of such compounds or salts, as dyeing or printing agent.

* * * * *

35

40

45

50

55

60

65